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Cationic Polymeric Microparticle Flocculant for Precipitated Calcium Carbonate

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CATIONIC POLYMERIC MICROPARTICLE FLOCCULANT FOR PRECIPITATED CALCIUM CARBONATE

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ABSTRACT

A serious of cationic polymeric microparticles (CPMP) with different charge density and particle size were synthesized using emulsion polymerization and microemulsion polymerization techniques. The interactions among positively charged polymeric microparticles, negatively charged fibers, and precipitated calcium carbonate (PCC) particles were studied. The results support microparticle bridging flocculation mechanism. The bridge formation between CPMP and PCC particles as a function of surface charge was examined. The addition of anionic polyelectrolyte, such as poly(acrylic acid) (PAA), would significantly affect PCC flocculation. Different bridging mechanisms were proposed based on the experimental results.

RÉSUMÉ

Une série de microparticules cationique (CPMP) de taille et de densité de charge différentes ont été synthétisées par des techniques des polymérizations par émulsion et microémulsion. Les interactions entre les microparticules de charge positive, les fibres de charge négative et les particules de carbonate de calcium précipité (PCC) ont été étudiées. Les résultats supportent le mécanisme de flocculation par pontage des microparticules. L'effet de la charge du surface sur le pontage des particules de charge opposées a été étudié. L'addition de polyeléctrolyte anionique, comme le poly(acide acrylique) (PAA), devrait affecter significativement rétention du PCC. Différents mécanismes de pontage ont été proposés à partir des résultants expérimentaux.

INTRODUCTION

In the last decade, the shift from acid to alkaline paper has largely taken place in the paper industry since there are many advantages to use precipitated calcium carbonate (PCC) over the traditional acid papermaking using aluminum sulfate and clay. However, the retention of fillers, fines, and other additives in alkaline condition has been found to be more difficult than it was in traditional acid papermaking. To overcome poor retention, many new techniques and retention systems, such as dual retention aids[1], micropolymer retention aids[2], and microparticle retention aids[1], have been brought into the paper industry. Although these new systems greatly improved pulp retention, the mechanisms have not been well studied. In addition to the fundamental study, some practical problems, such as the deposition of solid materials on wire, poor sizing ability, and economic problems, have not been well solved in alkaline papermaking.

Cationic polyelectrolytes, including linear, graft, and crosslink polymers, have been used extensively in fields such as papermaking, painting, water purification, oil recovery, mineral processing, and biological material separation [3-6]. Among these applications, using polyelectrolytes as flocculants in aqueous solution is one of the most important categories.

Flocculation is a universal phenomenon of thermodynamic unstable suspension systems. However, to achieve an effective flocculation rate and degree, a flocculant is generally needed. The flocculation of negatively charged particles, such as clays, silica, latex, and cellulose materials, by oppositely charged polymers has been extensively studied [7-14]. Different mechanisms, such as charge neutralization, hetero-coagulation, patching formation, bridging, and complex network formation, have been suggested.

It has been known that both kinetic and thermodynamic processes will affect the floc formation when a cationic polymer is used. The most important kinetic properties are the rate of the adsorption and the initial structure of adsorbed polymer. The loop length of polymer on solid surfaces is a critical factor affecting the bridging flocculation since an effective flocculation can be obtained only when the loop length is long enough to overcome the repulsion force between two charged particles.

It is known that, for an effective bridging flocculation, (1) the polymers must be adsorbed on the suspension surfaces, and (2) the loops of adsorbed polymer

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molecules must be long enough. The former requires a high charge density of polyelectrolyte to generate strong attractive forces between polymers and particles, and the latter requires a low charge density of polyelectrolyte to form extended polymer loops. The conflict of requirements between (1) and (2) suggests that the polymer must have an optimized charge density if it is used as flocculant. Both theoretical calculations [15] and experimental studies [16-18] indicated that high charged polymers adsorb in a flat configuration rather than an extended polymer chain. Instead of water soluble polymers, a positively charged microparticle flocculant may be a good choice to increase both charge density and bridge length simultaneously because of its fixed structure.

Although many people may consider soluble polymeric coagulants and flocculants significantly more effective than particle flocculants, it has been found [19-20] that microparticles are very effective retention aids, particularly in alkaline papermaking. It has been reported [21-23] that negatively charged microparticle retention systems can improve the paper formation, water drainage, and retention efficiency. Although these negatively charged microparticles combining with positively charged cationic polymers have been widely used in paper industries, the cationic polymeric microparticle has not been studied as a retention aid in alkaline papermaking.

The fundamentals of particle bridging flocculation have been studied previously by Vincent et al. [24,25]. A temperature-sensitive particle flocculant has been reported recently by Deng and Pelton [26,27]. It was found [26,27] that microparticle bridging flocculation was more effective and less concentration-dependent compared to the neutralization flocculation using water soluble polyelectrolytes.

Potentially, cationic polymeric microparticles have some advantages over soluble polyelectrolytes because: 1) there is almost no configuration change when the CPMP adsorbs on a negatively charged substrate ; 2) the bridge length can be exactly controlled by the particle size ;and 3) the charge density can be easily controlled. They also have advantages compared to positively charged inorganic microparticles, such as alum, because the polymeric microparticles can be used at higher pH. In this study a series of well-defined cationic polymeric microparticles as flocculants for PCC suspension in alkaline condition were examined, and the flocculation mechanisms in different solutions were studied.

EXPERIMENTAL

Materials

Styrene (Aldrich) was distilled to remove inhibitors before use. Methacrylamidopropyltrimethylammonium chloride (MAPTAC, 50% aqueous solution, Polysciences Inc.) was used as a cationic monomer to provide a positive charge for microparticles. Divinylbenzene (DVB, Aldrich, 55% solution) was used as a crosslinker. The initiator, 2,2'-azobis(N,N'-dimethylene-isobutyramidine)dihydro-chloride (VA-044) , was provided by Wako Pure Chemicals. Cationic surfactant, mistryltrimethyl-ammonium bromide, was used as an emulsifier. The cationic monomer, crosslinker, initiator, and emulsifier were used as purchased.

Poly(dialyldimethylammonium chloride) (poly-DADMAC, Polyscience Inc., 15% solid) was used as water soluble cationic polyelectrolyte. The charge density of the polymer, determined by colloid titration, was 1274 mgeq/g. Poly(acrylic acid) (PAA) was a linear polymer with an average molecular weight of 200,000 g/mol.

Precipitated calcium carbonate (PCC, Specialty Minerals Inc.) was a scalenohedral calcite filler product (Albacar HO, Specialty Minerals Inc.) with an average particle size of 1.3 microns and specific surface area of 12 m^2 /g.

Cellulosic fibers used were once-dried bleached kraft soft wood pulp. Clean fibers were prepared by washing the pulp with deionized water followed by Büchner funnel filtration three times. The absence of water soluble polymers in pulp after washes was confirmed by colloid titration of the supernatant of the pulp.

Preparation of CPMP:

The cationic polymeric microparticles with variable charge density and particle size were prepared using emulsion or microemulsion polymerization. A typical example of polymerization (for sample C, see **Table I**) was given as follows : A double-wall glass reactor equipped with mechanical stirrer, was filled with 150 ml of deionized water, 0.108 mol of styrene, 0.0043 mol of DVB, 0.0019 mol MAPTAC ,and 0.0089 mol cationic surfactant. The solution was flashed with nitrogen for 30 min. and thermostated at 60 °C. After temperature equilibrium, 0.007 mol of VA-044 in 5 ml of deionized water was added. The polymerization was carried out under nitrogen at stirring speed of 500 rpm for 4 hours. The cationic polymeric microparticles were centrifuged

twice (60,000 rpm, Beckman L-80 ultracentrifuge) for 120 minutes to remove cationic surfactant, excess monomers, and water-soluble polymers.

Physical property measurements

Flocculation: The flocculation of PCC suspension in water or pulps was determined as follows. The PCC sludge was added into a 80 ml test tube and then diluted to 0.05 wt-% using water or pulp. The final volume of PCC was adjusted to 50 ml using deionized water. The required amount of CPMP, poly-DADMAC, or PAA solution was added and the mixture was immediately shaken for another few seconds. The mixture was allowed to stand for 10 minutes at room temperature. 5 ml solution was carefully pipeted from the top and the transmittance was measured using Shinazu UV160U spectra photometer at a wavelength of 550 nm. Deionized water was used as a reference (transmittance = 100%) and the suspension without adding any polymer was used as a control solution. The relative turbidity, τ/τ_0, was used to determine the flocculation ability of microparticles or polymers, where τ and τ_0 are the turbidities of the solution with and without flocculant (control solution), respectively.

Zeta potentials: The zeta potential was measured using a Zetasizer 2c (Malvern) at a stationary position. The zeta potential of fines was assumed to be representative of fibers.

Particle size: The particle sizes of cationic polymeric microparticles were determined by Doppler Electrophoretic Light Scattering (Zetasizer2c, Malvern).

Colloid titration: The surface charge and concentration of CPMP were determined by colloid titration. Twenty ml of sample was prepared with 0.01 M KCl ionic buffer. After equilibrium, five drops of orthotruidineblue indicator solution and 10 ml of 0.005 N poly-DADMAC were introduced and the suspension was titrated to the colometric end point with polyvinylpotassiumsalfate.

Adsorption isotherm: The adsorption of CPMP by PCC was measured at pH of 9.3 and room temperature. 5g/L PCC was mixed with required CPMP for 4 hours. The CPMP concentration of supernatant was determined by colloid titration using a concentration calibration curve.

RESULTS AND DISCUSSIONS

Microparticles

The microparticles used in this study were prepared by emulsion polymerization in the presence and the absence of cationic surfactant. The properties of the latexes are given in **Table I**. A typical example of the latex preparation and cleaning process has been given in the experimental section.

Generally speaking, both size and electrostatic properties of the microparticles are a function of the concentrations of surfactant, crosslinker, cationic monomer, and temperature. The details of polymerization and characterization of microparticles will be given in separated papers.

TABLE I. MICROPARTICLE PREPARATIONS AND THE COLLOIDAL PROPERTIES

Sample	A	B	C	D	E
Styrene (mol)	0.108	0.108	0.108	0.108	0.108
MAPTAC (mol)	0	0	0.0019	0.0113	0.0338
C-surfactant (mol)	0	0.0089	0.0089	0.0089	0.0089
water (L)	0.150	0.150	0.150	0.150	0.150
VA-044 (mol)	0.0007	0.0007	0.0007	0.0007	0.0007
DVB (mol)	0	0.0043	0.0043	0.0043	0.0043
Particle size (nm)	178.2	28.7	33.9	42.3	52.5
Polydispersity	0.17	0.17	0.24	0.41	0.34
Charge density (ugeq/m^2)		4.64	4.97	5.87	4.78

Flocculation of PCC Caused by CPMP Alone

Since both PCC and CPMP are charged particles, the forces between these two particles strongly depend on the sign and the charge density of the particle surfaces.

The dependence of zeta potential upon pH for CPMP, PCC, and clean fibers (water soluble and colloidal materials had been removed by washes before measuring the zeta potential) was investigated and the results are shown in **Figure 1.** It can be seen that the PCC has an isoelectric point (i.e.p.) at pH of 10.5. In contrast to the PCC, the zeta potential of the clean fibers is negative in the whole pH range and slightly decreases as pH is increased. It can also be seen that the zeta potential of the cationic polymeric microparticle (sample A) slightly decreases with the increase of pH up to 9.8, and sharply dropped as PH further increased. Since sample A was prepared in the absence of cationic monomer, the slight decrease of zeta potential of CPMP with pH may be attributed to the hydrolization of the polymer end groups which were introduced by the cationic initiators during the polymerization.

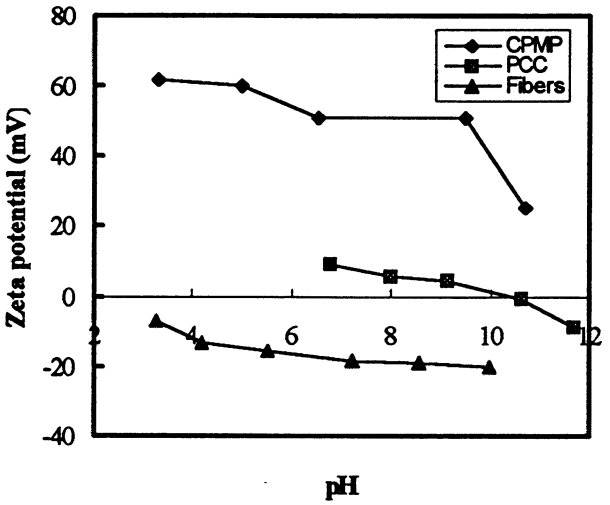

Figure 1. Zeta potentials of CPMP (sample A), PCC, and fibers as a function of pH.

The flocculation of PCC suspension by CPMP in various conditions was investigated by turbidity measurement. **Figures 2** and **3** show the relative turbidity of PCC suspension as a function of the concentrations of CPMP (sample D) and poly-DADMAC, respectively. **Figure 2** indicates that the addition of CPMP resulted in only a small change in relative turbidity (from 1 to 1.15). This small increase in the relative turbidity may be attributed to the formation of a few tiny PCC aggregates which did not sedimentate during the measurements period (10 min.). The very small change in relative turbidity for this system indicates that CPMP alone is not an effective flocculant. Although the adsorption of CPMP on the positively charged PCC surfaces has been confirmed (see below), the poor flocculation of PCC by CPMP is expected because (1) both PCC and CPMP are positively charged in water so that the adsorption of CPMP on PCC surface is not strong, and (2) the particle size of CPMP is only 42.3 nm which is not long enough to overcome the repulsion force between two positively charged PCC particles.

It is interesting that although the relative turbidity of the PCC-CPMP system remains almost a constant (see **Figure 2**), the zeta potential of the PCC suspension increases sharply from 5 mV to 28 mV as the CPMP concentration

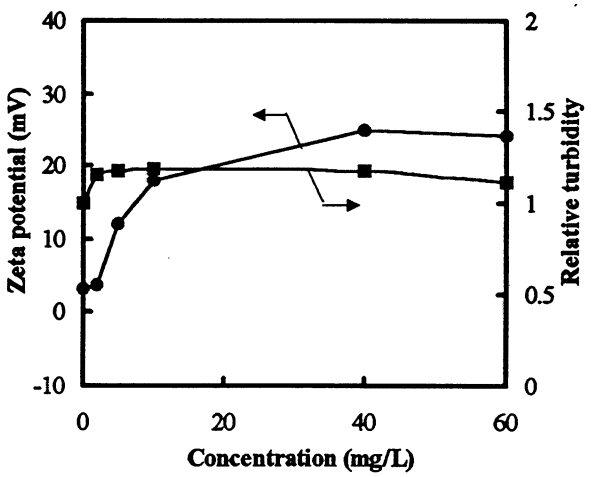

Figure 2. Zeta potential and relative turbidity of PCC suspension as a function of CPMP (sample D) concentration at pH of 8.9. PCC consistency: 0.05%

increases from 0 to 40 mg/L. The increase of zeta potential suggests an effective adsorption of CPMP on the PCC surfaces although both of them were positively charged. The adsorption of CPMP on the positively charged PCC was further confirmed by adsorption measurement (see below). One of the possible reasons for positively charged microparticle adsorbs onto positively charged solid substrate may be due to the exchange reaction between adsorbed Ca^{2+} and CPMP on the PCC surface.

In comparing with the flocculation efficiency using cationic polymeric microparticles, **Figure 3** shows the relative turbidity of PCC suspension as a function of poly-DADMAC. A sharp decrease in relative turbidity as

the concentration of poly-DADMAC changing from 0 to 2 mg/L was observed, which indicated a significant flocculation of PCC. Since there is no charge neutralization between PCC and poly-DADMAC (both are positively charged), the flocculation at this low polymer concentration can only be attributed to the formation of extended poly-DADMAC bridge between PCC particles. When the concentration of poly-DADMAC is further increased , the relative turbidity increases to the same value as the reference ($\tau/\tau_0 = 1$). The increase of relative turbidity with further increase of poly-DADMAC concentration was due to the restabilization of PCC by adsorbed polyelectrolyte.

It has been known that the surface charge of PCC particles is a function of the concentration of Ca^{2+} and CO_3^{2-} in the solution. The relationships between zeta potential and concentrations of Ca^{2+} and CO_3^{2-} are shown in **Figure 4**. Since the zeta potential of PCC is negative at high concentration of sodium carbonate, the attractive force between positively charged CPMP and negatively charged PCC is stronger than the attractive force if they are dispersed in pure water. As a result, an effective flocculation of PCC caused by CPMP bridging is expected. This is confirmed by turbidity measurements shown in **Figure 5**. It can be seen that in a 5 mM

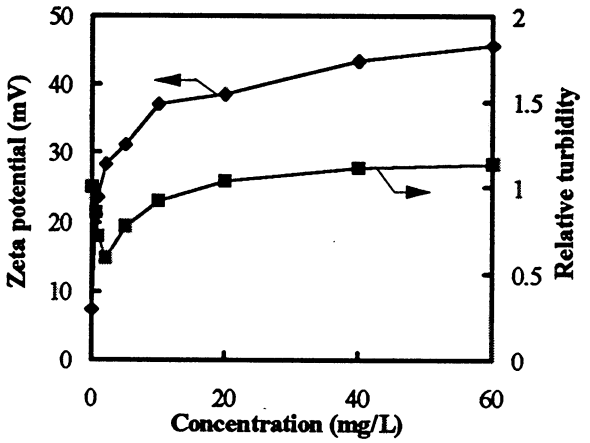

Figure 3. Zeta potential and relative turbidity of PCC suspension as a function of poly-DADMAC concentration at pH 8.9. PCC consistency: 0.05 wt-%.

Na_2CO_3 solution, the relative turbidity of PCC sharply decreases then slightly increases as the concentration of CPMP is increased. Comparing the results of **Figure 2** and **Figure 5** , it is concluded that the flocculation of PCC by CPMP strongly depends on the surface charge of PCC particles.

Flocculation of PCC Caused by CPMP-PAA Dual Flocculants

Since PCC particles are negatively charged in wood pulp due to the adsorption of anionic polymers, it is interesting to know how these negatively charged water-soluble polymers will affect the PCC flocculation if CPMP is used as flocculant. In this study, PAA was used as a model water-soluble anionic trash in pulps. In order to separately study the effects of adsorbed and free anionic PAA on the flocculation of PCC, the PAA was added to the systems in different sequences. For a PAA-modified PCC system, PAA was first mixed with PCC suspension to allow PAA adsorbing on PCC surface before adding flocculant CPMP. The free PAA in PCC-PAA mixture was then washed out using deionized water leaving only strongly bonded PAA on the PCC surface. This PAA modified PCC showed strong negative charge in deionized water. The PAA-modified PCC was redispersed in water (0.05 wt-%) followed by the addition of the flocculant of CPMP. The zeta potential and the relative turbidity of this system as a function of CPMP concentration are shown in **Figure 6**. It can be seen that the relative turbidity of PCC in this system is lower compared to the relative turbidity of unmodified PCC suspension (**Figure 2**), which suggests a remarkable flocculation of PAA-modified PCC was caused by CPMP. Visual observation indicated that the flocculation of this system was fast and the flocs were larger than unmodified PCC. Since there was no free PAA in the solution (confirmed by colloidal titration), the flocculation of PCC particles was only attributed to the bridge formation through positively charged CPMP.

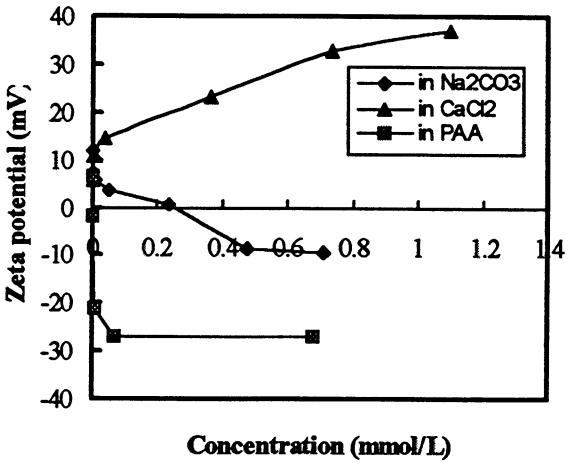

Figure 4. Zeta potential of PCC as a function of the concentrations of Na_2CO_3, $CaCl_2$, and PAA at pH 9. The zeta potentials for PCC-PAA system was obtained after washing three times using deionized water.

The effect of surface charge on the PCC flocculation is summarized in **Figure 7**. It is interesting to note that the sequence of polymer addition can significantly affect the flocculation efficiency. For example, curve **C** shows the results of adding PAA first , followed by washing the sample, then adding the CPMP. Curve **D** shows the results of adding CPMP first followed by the addition of PAA. Both visual observation and turbidity measurement indicated that a more effective flocculation could be obtained if CPMP was added first followed by

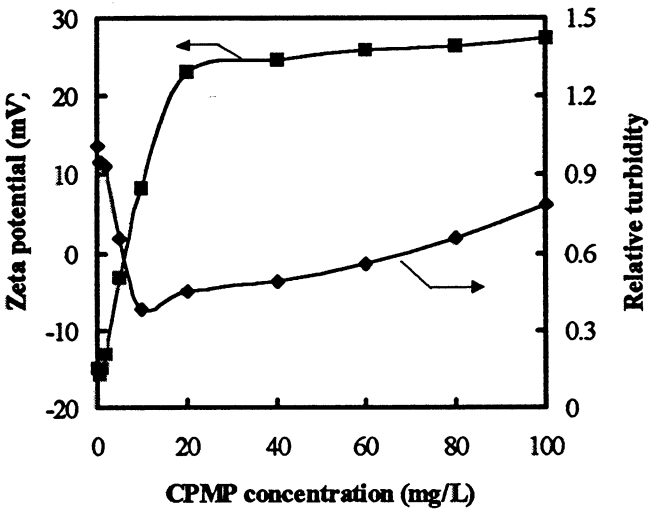

Figure 5. Relative turbidity and zeta potential of PCC suspension in 0.47 mmol/L sodium carbonate as a function of CPMP (sample D) concentration.

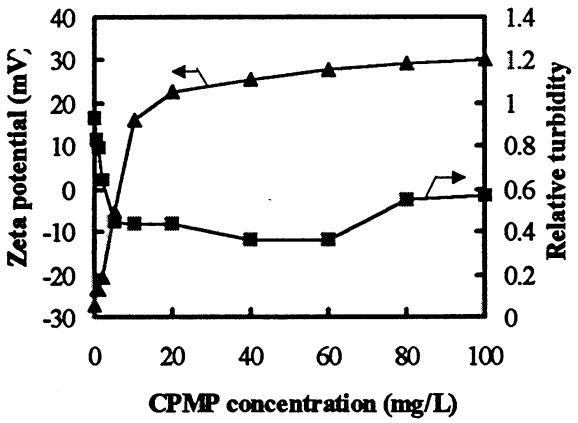

Figure 6. Relative turbidity and zeta potential of PAA- modified PCC as a function of CPMP (sample D) concentration. PCC was mixed with 1 wt-% PAA (based on PCC), and then washed three times using deionized water. PCC consistency: 0.05 wt-%.

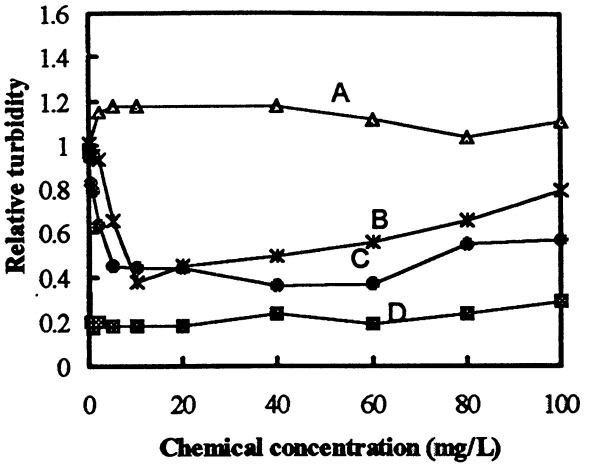

Figure 7. Relative turbidity of PCC suspension as a function of chemical addition. A: PCC and CPMP in water; B: PCC and CPMP in 0.47 mmol/L Na_2CO_3 solution; C: CPMP was added into PAA modified PCC; D: CPMP was added into PCC before adding PAA.

PAA. We believe that the different addition orders will lead to different flocculation mechanisms. The mechanisms which correspond to curves **A** to **D** in **Figure 7** are schematically shown in **Figures 8A to 8D**.

Figure 8-A shows the interaction between CPMP and PCC particles in water (corresponding to the curve A in **Figure 7**). Since both the PCC and the CPMP are positively charged in this condition, the repulsion force between two PCC particles is strong enough to prevent the approach of the particles. In this case, the bridging flocculation is almost ineffective.

Figure 8-B shows the interaction between PCC and CPMP in sodium carbonate solution (corresponding to the curve B in **Figure 7**). Since PCC is negatively charged in this solution, there is a relatively strong attractive force between PCC and CPMP. This attractive force results in a strong adsorption of CPMP on the PCC surface. As a result, effective bridges between PCC particles are formed through adsorbed CPMP particles.

Figure 8-C shows the bridge formation in PAA-CPMP dual flocculant system where PCC was first modified by PAA (corresponding to the curve C in **Figure 7**). It can be seen that the adsorbed PAA plays two roles: modifying the surface charge of PCC and forming a co-bridge with CPMP. Since the length of the bridge is increased comparing to the bridge length of single CPMP, a more

Figure 8-A:

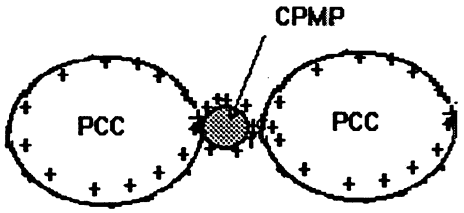

Figure 8-B:

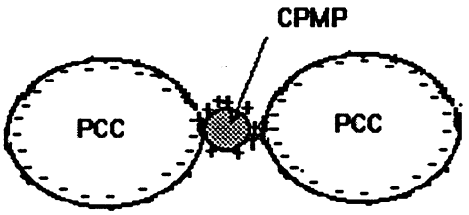

Figure 8-C

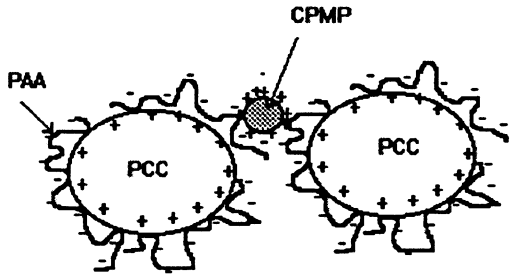

Figure 8-D:

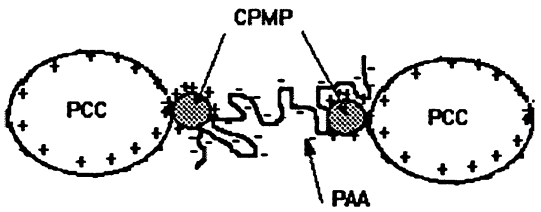

Figure 8. Proposed flocculation mechanisms. A: PCC and CPMP in water; B: PCC and CPMP in Na_2CO_3 solution; C: CPMP was added into PAA-modified PCC; D: CPMP was added into PCC before adding PAA.

effective flocculation is expected in this dual flocculant system.

Figure 8-D shows the bridge formation in CPMP - PAA system but CPMP is added before PAA (corresponding to the curve D in **Figure 7**). Since two CPMP particles are involved in the same bridge, the distance between the two PCC particles is longer than that shown in **Figure 7C**. As a result, the flocculation is further improved. All suggested mechanisms shown in **Figures 8A** to **8D** are consistent with experimental results shown in **Figure 7**. Although more studies are needed to conduct the detail structures of the floc formation in those systems, the results obtained in this study clearly show that the bridge formation strongly depends on the surface charge and the soluble polyelectrolytes in the suspension. We believe that the principles conducted in this study using cationic polymeric microparticle system can also be applied to the other systems, such as filler retention in alkaline papermaking using negatively charged microparticles and positively charged water-soluble polymers.

The Effect of Fibers on PCC Flocculation

It is well known that commercial fibers contain soluble anionic materials such as fatty acids and low molecular weight lignin. These anionic polymers will adsorb onto fiber, fine, and PCC surfaces. In order to evaluate the interaction among PCC, CPMP, and fibers, a clean bleached kraft fiber furnish (extensively washed with

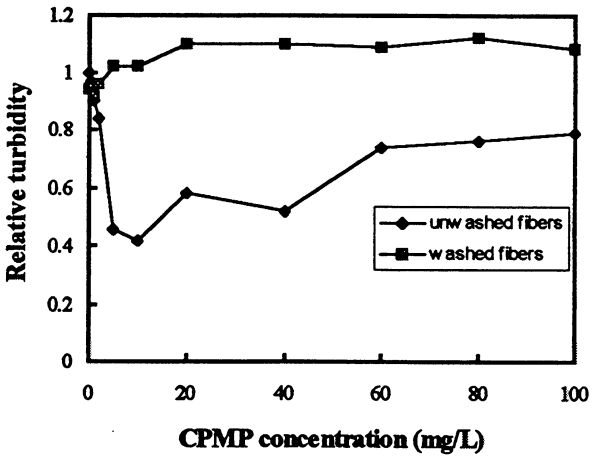

Figure 9. Relative turbidity as a function of PCC concentration in washed and unwashed fibers.

deionized water) was compared with a commercial bleached fiber furnish (unwashed fibers). Zeta potential measurement indicated that both washed and unwashed fibers had strong negative charges. However, the surface charge of PCC in these two pulps is different: it is positively charged in washed pulp and negatively charged in unwashed pulp.

Since the surface charge of PCC in washed and unwashed pulp have different signs, the flocculation of PCC by CPMP in these two pulps must be different. **Figure 9** shows the relative turbidity of PCC suspension in these two pulps as a function of CPMP concentration. It can be seen that the clean fibers only slightly affect the flocculation of PCC (when relative turbidity is almost one), but anionic trash in unwashed pulp significantly increases the flocculation of PCC if CPMP is used as flocculant. Although the mechanism of PCC flocculation by CPMP in unwashed furnish cannot be conducted from the results of turbidity measurement alone, it is clear that dissolved negatively charged polymers will contribute remarkably to the interaction among PCC, CPMP, and fibers. Scanning electron microscopy showed that PCC particles were directly bounded on fiber surface when CPMP was added.

Adsorption Isotherm

The adsorption isotherm of positively charged CPMP on positively charged PCC was measured and the results are shown in **Figure 10**. It can be seen that both zeta potential and adsorption amount of PCC particles sharply increases initially and then gradually flattens as the CPMP concentration is increased. At CPMP addition of 200 mg(g PCC)$^{-1}$ the adsorption of CPMP reaches a constant value. From adsorption isotherm, the fractional coverage θ_A of CPMP on the PCC surface can be calculated:

$$\theta_A = \frac{n\pi r^2}{S_A} = \frac{\frac{\Gamma}{v\rho}\pi r^2}{S_A} = \frac{3\Gamma}{4r\rho S_A} \quad \text{.....} \quad (1)$$

Where n is the number of CPMP per gram PCC, r is the radius of microparticle (21.15×10^{-9} m for sample D), S_A is the specific area of PCC (12 m^2/g), Γ is the saturated adsorption amount of microparticles on the PCC surface (14×10^{-3} g/g), V is the volume of one CPMP particle (m^3), and ρ is the density of microparticles (assuming equal to the density of polystyrene, 1.1×10^6 g/m^3), respectively. Substituting these data into equation (1) gives that the fractional coverage, θ_A, of CPMP on PCC surface at pH 9.3 is only 0.038. This is extremely small comparing with most water-soluble polyelectrolyte adsorbing on an opposite-charged substrate. This supports the finding that the adsorption of positively charged CPMP on positively charged PCC is not significant although zeta potential of PCC suspension was found to increase significantly.

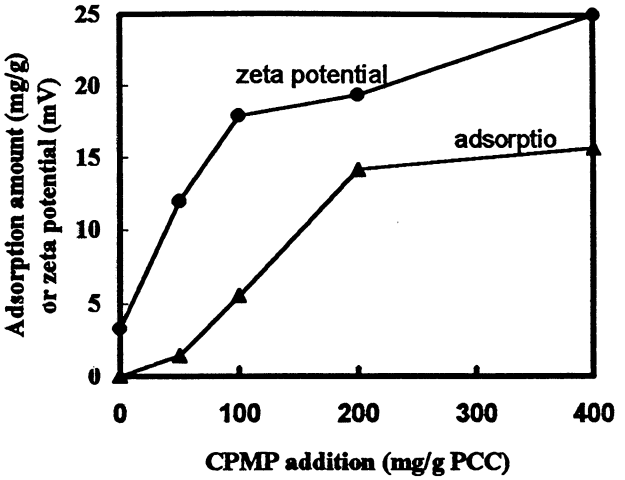

Figure 10: Adsorption isotherm of CPMP (sample D) on the PCC surface and the zeta potential of PCC as a function of CPMP concentration at pH of 9.3.

CONCLUSIONS:

Cationic polymeric microparticles with a broad surface charge and particle size can be synthesized using emulsion and microemulsion polymerization techniques. The surface charge of the microparticle is positive up to pH 11. These cationic polymeric microparticles can be adsorbed on PCC surface in water at alkaline pH, but the adsorption is not strong. The CPMP is not an effective flocculant for positively charged PCC if it is used alone. However, the flocculation efficiency can be improved if the PCC surface is modified to a negative charge, such as by addition of sodium carbonate or PAA in the suspension. The presence of a water-soluble anionic polymer will significantly affect the flocculation of PCC if CPMP is used as flocculant. Varying the sequence of polymer addition will lead to different flocculation mechanisms, which will significantly affect the flocculation efficiency. Four different bridging mechanisms were proposed based on the experimental results obtained in this study.

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